

Large Infrared Nonlinear Optical Response of C₆₀

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C₆₀ buckminsterfullerene exhibits a large ultrafast third-order nonlinear optical response. Degenerate four-wave-mixing measurements in C₆₀-benzene solutions were performed using 50-psec pulses at 1.064 μm. The magnitude of the nonlinear susceptibility per C₆₀ molecule is $|\gamma| = 1.5 \times 10^{-42} \text{ m}^5 \text{ V}^{-2}$ and of the same size as that observed in polydiacetylene. In contrast to conjugated polymers, however, a dominant positive real part of the nonlinearity is found, 3 times larger than the imaginary component. The nonlinear response can be described within the model of a free electron in a spherical box, confirming the complete delocalization of electrons on the C₆₀ molecule.

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Confinement of free or quasifree electrons on a nanometer scale has received considerable interest in optics recently [1]. In semiconductor nanoparticles, for example, carrier confinement leads to a singularity in the density of states at the band gap which in turn gives rise to an enhanced nonlinear optical response near the associated optical transition compared with nonconfined materials [2]. Such particles are commonly termed quantum dots. On the other hand, conjugated polymers such as polyacetylene and polydiacetylene show sizable ultrafast nonlinearities due to the one-dimensional nature of the delocalized π electrons [3]. Fullerenes [4–9] also possess highly delocalized electrons and so are expected to exhibit nonlinear optical behavior similar to conjugated polymers. In addition, however, the three-dimensional nature of the particles should also be apparent in this response. In this Letter we report the observation of infrared nonlinear optical response of C₆₀-buckminsterfullerene-benzene solutions which shows some similarity with that of conjugated polymers. As a result of a dominant real part of the nonlinearity and the relatively small size of the molecule, however, more favorable solid-state properties can be expected, making this class of materials interesting candidates for nonlinear optical devices.

C₆₀ buckminsterfullerene was prepared and purified as described in the literature [8,9]. Magenta solutions up to a maximum concentration of 500 mg/L were prepared in benzene. The absorption spectra of the samples are complex consisting of a series of closely overlapping peaks between 450 and 700 nm with a first absorption maximum near 593 nm. In general, the similarity of this spectrum with that of 3-BCMU polydiacetylene in chlorobenzene should be noted [10].

Nonlinear optical measurements were performed using the forward degenerate four-wave-mixing technique as described elsewhere [11]. The laser used was a passively

mode-locked amplified Nd-doped yttrium-aluminum-garnet laser emitting 50-psec pulses at 1.064 μm of up to 5 mJ energy. This technique is based on diffraction from nonlinear optically induced transient gratings and allows the magnitude of the nonlinear optical response to be measured. The observed response corresponds to a modulation of the material's refractive index associated with the light-induced polarization of the delocalized electrons. In centrosymmetric materials, such as buckminsterfullerene, the induced polarization can be described by [12]

$$P_{\text{ind}} = \epsilon_0 \chi^{(3)} E^3, \quad (1)$$

where $\chi^{(3)}$ is the third-order nonlinear susceptibility, E the applied electric field of the laser pulse, and ϵ_0 the permittivity of free space. Therefore $\chi^{(3)}$ provides a measure of the magnitude of the cubic nonlinear response. In molecular systems it is usual to normalize the nonlinearity to one molecule, in which case one obtains the hyperpolarizability γ from

$$\gamma = \chi^{(3)} / NL^4, \quad (2)$$

where N is the density of molecules per unit volume and L is the Lorentz field factor associated with the shielding of the electric field experienced by the molecule in its local environment. Experimentally one observes the diffraction efficiency η of the laser-induced grating which corresponds to $(P_{\text{ind}}/E)^2$. The cubic nonlinear susceptibility can be derived by comparing the intensity dependence of the diffraction efficiency with that of a material of known nonlinear response such as neat benzene ($\chi^{(3)} = 2 \times 10^{-21} \text{ m}^2 \text{ V}^{-2}$) [9]. As the intensity I is proportional to E^2 , η depends quadratically on I as shown in Fig. 1 for a 15-mg/L solution of C₆₀ buckminsterfullerene. This confirms that the nonlinear response originates from a third-order susceptibility. By accounting for

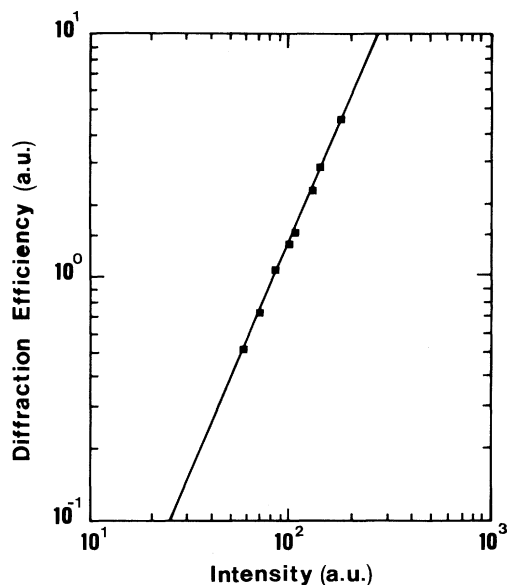


FIG. 1. Intensity dependence of the diffraction efficiency of the laser-induced grating in a 15-mg/L solution of C_{60} buckminsterfullerene in benzene. The solid line is a fit with a slope of 2, typical of a third-order nonlinear susceptibility.

concentration effects as described below, the magnitude of the hyperpolarizability of a C_{60} molecule can be calculated and is found to be $|\gamma| = (1.5 \pm 0.3) \times 10^{-42} \text{ m}^5 \text{ V}^{-2}$. It is again interesting to note that this value is similar to that of polydiacetylene solutions ($|\gamma| = 2.0 \times 10^{-42} \text{ m}^5 \text{ V}^{-2}$) [13]. The temporal decay of the nonlinearity was investigated with the same laser using a phase-conjugation setup [12]. It was found to decay within the pulse width of 60 psec.

The optical nonlinearity consists of both a real and an imaginary component. The imaginary part accounts for changes in absorption (saturable or induced) whereas the real part constitutes a change in refraction. Organic solvents such as benzene only possess a real positive nonlinear response originating from the optical Kerr effect [12]. By observing the dependence of the total nonlinear response of a solution as a function of solute concentration it is possible to derive both the sign and magnitude of the real part and the magnitude only of the imaginary part of γ [13]. Figure 2 shows the dependence of the square of the susceptibility on the concentration, which should be a parabola. Obviously the real part of the nonlinearity has the same sign as the solvent response and is therefore positive. At high concentrations a leveling off of the concentration dependence can be seen, which is frequently observed in molecular systems and indicates a strong tendency for aggregation of the solute. By fitting the dependence as described in Ref. [13] one obtains a ratio of the real to the imaginary part as $\gamma_R/\gamma_I = 3.2$, i.e., the real part dominates. This behavior is different from that of conjugated polymers where the imaginary com-

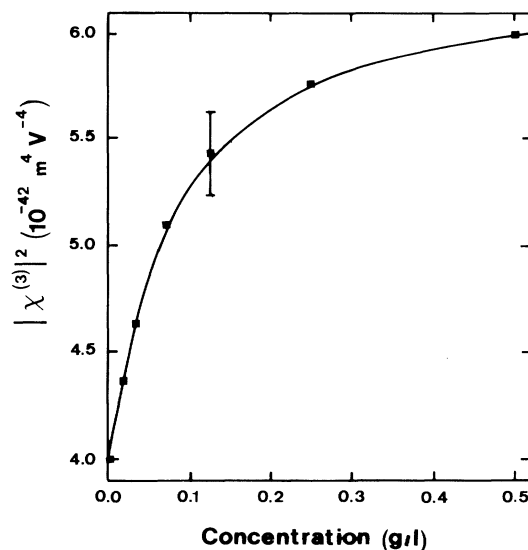


FIG. 2. Concentration dependence of the nonlinearity of C_{60} buckminsterfullerene in benzene.

ponent is usually at least the same magnitude as the real [13].

The similarity between the nonlinear optical behavior of C_{60} buckminsterfullerene and typical conjugated polymers may be attributed to the fact that the electrons in both systems are substantially delocalized. A simple model for the optical response of conjugated carbon chains was proposed by Rustagi and Ducuing [14]. The molecules were treated as one-dimensional boxes containing delocalized π electrons. This so-called "free-electron" model predicts a large real nonlinearity away from optical absorption bands. Because of the fact that imaginary components sometimes dominate in conjugated polymers, this model does not always lead to a quantitative understanding of the nonresonant processes in polymers. It is simple to extend this model to describe delocalized electrons on a spherical surface. By solving the Schrödinger equation of this system we obtain an expression for the energy levels of the electrons which correspond exactly to the simple one-dimensional solution. Following the procedure outlined in Ref. [14] one can calculate the hyperpolarizability of the sphere by fourth-order perturbation theory as

$$\gamma = \frac{128L^{10}}{a^3 e^2} \sum_{n=1}^N \left[-\frac{2}{9\pi^6 n^6} + \frac{140}{3\pi^8 n^8} - \frac{440}{\pi^{10} n^{10}} \right], \quad (3)$$

where L is the circumference of the sphere, a the width of the electron shell, e the electron charge, and N the total number of delocalized electrons ($N=60$). γ is completely real and, for large N , positive. Taking a circumference of $L=22 \text{ \AA}$ derived from standard bond lengths and spherical geometry and an electron shell width of 2.5 \AA into account, the position of the first absorption max-

imum can be calculated to be 550 nm and the hyperpolarizability to be $\gamma = 2 \times 10^{-42} \text{ m}^5 \text{ V}^{-2}$ from Eq. (3). This is in good agreement with the experimental data, and therefore suggests the existence of a delocalized π -electron system around the surface of the nearly spherical C_{60} buckminsterfullerene as also indicated by the increase in electrical conductivity and the detection of superconductivity in doped material [15]. The increase in the ratio of the real to the imaginary part of the nonlinearity compared with that in conjugated polymers is consistent with a decrease in the electron-vibration coupling characteristic of a more rigid spherical molecular system. Such a feature is most desirable for applications in integrated nonlinear optical devices. In addition, the magnitude of the nonlinearity in the solid state can be extrapolated from the solution data and is expected to be approximately $10^{-16} \text{ m}^2/\text{V}^2$ ($\approx 10^{-8} \text{ esu}$). This is a remarkably large nonresonant value which should exceed those obtained from conjugated polymers. Initial measurements of nonlinear prism coupling in thin films of C_{60} yield a value $\chi^{(3)} = (6 \pm 4) \times 10^{-8} \text{ esu}$ in the solid state, which confirms the predictions from our solution data.

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